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Fiber-content dependency of the optical transparency and thermal expansion of bacterial nanofiber reinforced composites

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We produced transparent nanocomposite reinforced with bacterial cellulose having a wide range of fiber contents, from 7.4 to 66.1 wt %, by the combination of heat drying and organic solvent exchange methods. The addition of only 7.4 wt % of bacterial cellulose nanofibers, which deteriorated light transmittance by only 2.4%, was able to reduce the coefficient of thermal expansion of acrylic resin from 86×10^{-6} to $38 \times 10^{-6} \text{ K}^{-1}$. As such, the nanofiber network of bacterial cellulose has an extraordinary potential as a reinforcement to obtain optically transparent and low thermal expansion materials. © 2006 American Institute of Physics.

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Bacterial cellulose (BC), cellulosic nanofibers produced by bacteria, has extraordinary potential as a reinforcement to obtain optically transparent materials. Since bacterial cellulose nanofiber is a ribbon-shaped fiber of $10 \times 50 \text{ nm}$,^{1–4} it can be used to reinforce transparent plastics with less than 10% loss of light transmittance, even at fiber contents as high as 70 wt %.⁵ Because the nanofibers are made up of bundles of semicrystalline extended cellulose chains, their Young's modulus and tensile strength are 138 GPa (Ref. 6) and at least 2 GPa,⁷ respectively, and surprisingly, the thermal expansion in the axial direction is less than $0.1 \times 10^{-6} \text{ K}^{-1}$.⁸ Hence, this nanofiber reinforced composite showed incredibly low thermal expansion ($3 \times 10^{-6} \text{ K}^{-1}$) and high tensile strength (325 MPa), while maintaining the flexibility and ductility of many plastics.⁵ Besides, due to the nanofiber size effect, high transparency was obtained against a wide distribution of resin refractive indexes, from 1.492 to 1.636 at 20 °C.⁹ The optical transparency was also insensitive to temperature increases up to 80 °C.⁹ These nanofiber-network-reinforced polymer composites should lead the way to a wider use of optically transparent polymers in optoelectronic devices such as substrates for flexible displays and components for precision optical devices, which demand high transparency and low thermal expansion.

However, to further enhance the transparency of BC nanocomposites, maintaining their low thermal expansion and high strength, their optimum fiber-content must be elucidated based on the fiber-content dependency of the properties. Hence, in this Letter, we developed a method to produce BC composites in a wider fiber-content range and clarified the changes of regular light transmittance and the coefficient of thermal expansion (CTE) of the composites against fiber content.

BC pellicles with a thickness of 10 mm consisting of 1 vol % BC nanofibers and 99 vol % water were used as the

starting material.^{5,9} When the pellicles were pressed to one-tenth of their original thickness to squeeze out the water and then dried, the BC sheets shrank during the drying and their density became 1.0–1.2 g/cm³. As the density of the cellulose microfibrils is 1.6 g/cm³, the interstitial cavities in the dried sheets were estimated to account for 1/3–1/4 of the volume. Thus, when these cavities were completely filled by impregnating the sheets with neat acrylic resin [tricyclodecane dimethanol dimethacrylate (TCDDMA)] under a reduced pressure and cured by UV light,^{5,9} the fiber content of the BC nanocomposites was restricted to a range of 52.4–66.1 wt %.

To produce BC nanocomposites with lower fiber contents, it is necessary to prevent cohesion of BC nanofibers during the evaporation of water. Thus, organic solvents that are soluble in both water and acrylic resin were applied for the removal of water from BC pellicles instead of drying. That is, the BC pellicles were compressed, adjusting the thickness by a cold press to control the fiber content, and were dipped into a mixture of water and acetone, the concentration of which was increased from 50% to 100% step by step, to prevent nanofiber cohesion. Afterwards, the solvent-replaced sheets were impregnated with neat acrylic resin under reduced pressure and UV cured. The acetone was completely evaporated during the resin impregnation under reduced pressure. This method enabled the production of nanocomposites with lower fiber contents in a range of 19.0–49.0 wt %. The fiber contents of BC nanocomposites were determined by elemental analysis.

When ethanol was used as a solvent, due to its higher polarity, the thickness adjusted BC sheets swelled during the impregnation of acrylic resin. As a result, BC nanocomposites with fiber content in the range of 7.4–35.2 wt % were obtained. Consequently, the study of the fiber-content dependency of the optical transparency and thermal expansion of bacterial nanofiber reinforced composites became possible in a wider fiber-content range, from 7.4 to 66.1 wt %. The re-

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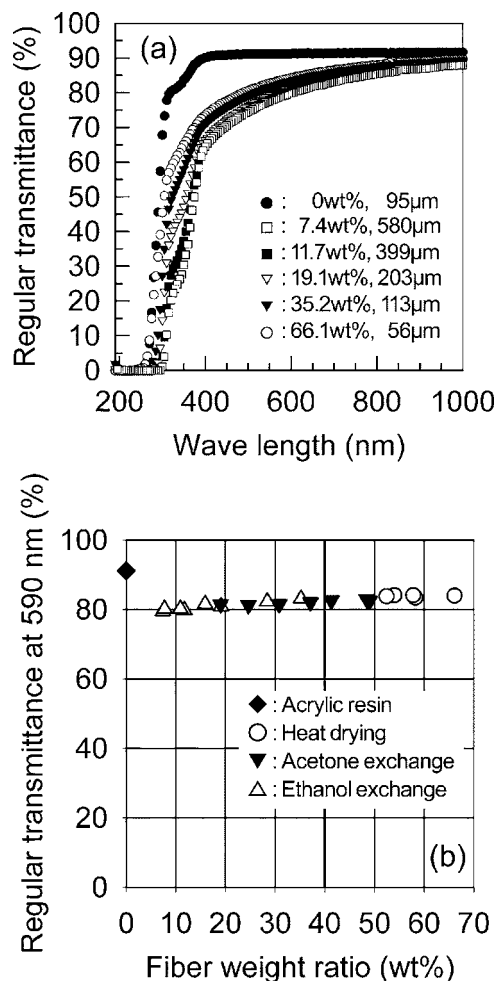


FIG. 1. Regular transmittance spectra (a) and the regular transmittance at 590 nm (b) of BC nanocomposite of various fiber contents (wt %) and thicknesses (μm).

sulting thickness of the composites was distributed from 56 to 580 μm .

Regular luminous transmittances were measured at wavelengths from 190 to 1000 nm using a UV-visible spectrometer with an integrating sphere 60 mm in diameter (U-4100, Hitachi High-Tech. Corp.). Regular transmittance was measured by placing the specimens 25 cm from the entrance port of the integrating sphere. The regular transmittances of BC nanocomposite sheets against various fiber contents are shown in Fig. 1. In Fig. 1(a), the regular transmittance spectra of acrylic resin and the BC nanocomposite produced by heat drying or by ethanol exchange are compared. All the composites absorb light below 400 nm affected by the optical characteristics of the acrylic resin and the transmittance gradually increases with increasing wavelength. Despite the wide distribution of fiber content and sample thickness as described above, all the BC nanocomposites transmitted more than 75% of the light in the wavelength of 500–800 nm, including Fresnel's reflection. However, careful comparison of the transmittance spectra against various fiber contents revealed an unexpected dependency; that is, the transmittance decreased in spite of the decrease in fiber content.

To investigate the dependency more precisely, the regular transmittances of BC nanocomposite at 590 nm were compared, as shown in Fig. 1(b). It was discovered that de-

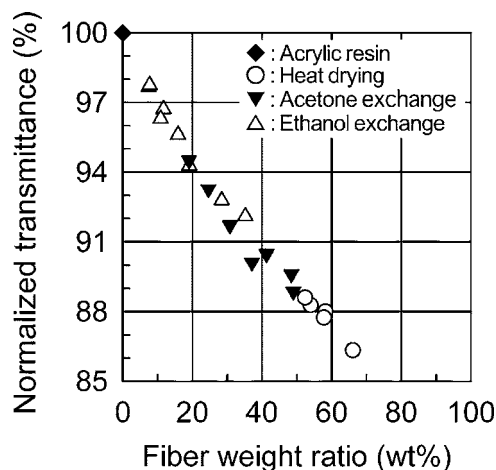


FIG. 2. Normalized regular transmittance at 590 nm and 100 μm thickness of BC nanocomposite against fiber content.

creasing the fiber content from 66.1 to 7.4 wt % leads to a reduction of the regular transmittance from 84.1% to 79.5%.

In the production of BC composites, fiber contents were adjusted by changing the thickness of the composite while maintaining the same amount of bacterial cellulose. The transmittances are influenced not only by their fiber contents but also by their thicknesses. Thus, to discuss the fiber-content dependency of the optical transparency excluding the effect of sample thickness, the regular transmittances at 590 nm of BC nanocomposites with 100 μm thickness were calculated by defining the regular transmittance of acrylic resin as 100%.¹⁰ As shown in Fig. 2, it was found that the normalized transmittance of BC nanocomposites increased against the decrease of fiber content linearly and regardless of the sample preparation methods.

Haraguchi and Usami reported that the light transmittance of a transparent phenolic resin sheet 100 μm thick deteriorated by 15% when 20 nm silica nanoparticles were well dispersed by 10 wt % using the sol-gel method.¹¹ Contrary to this, with BC nanocomposites, the reduction of the regular transmittance at the fiber content of 11.7 wt % was only 3.3% (Fig. 2). Even at fiber contents as high as 66.1 wt %, the loss of transparency was a mere 13.7% (Fig. 2). This clearly indicates that the bacterial cellulose has an extraordinary potential as a reinforcement to obtain optically transparent materials.

As mentioned above, lower fiber content is preferable from the viewpoint of high light transmittance of BC composites; however, decreasing fiber content could detract from the low CTE of BC composites. Hence, the CTEs of BC composites were evaluated against the fiber content. The CTEs were measured by a thermomechanical analyzer (TMA/SS6100, SII Nanotechnology Inc.). Specimens were 25 mm long and 3 mm wide with a 20 mm span. After heating at 180 $^{\circ}\text{C}$ for 2 h in a nitrogen atmosphere to postcure the acrylic resin, the measurements were carried out three times with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere in tensile mode under a negligible load of 3 mg to detect the thermal strain. The CTE values were determined as the mean values at 20–150 $^{\circ}\text{C}$ in the second run.

Surprisingly, the addition of only 7.4 wt % of BC nanofibers, which deteriorated light transmittance only by 2.4% (Fig. 2), could reduce the CTE of acrylic resin from 86×10^{-6} to $38 \times 10^{-6} \text{ K}^{-1}$ (Fig. 3). This is an excellent re-

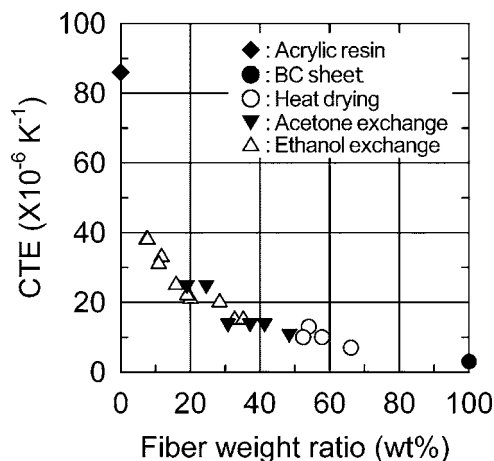


FIG. 3. The coefficients of thermal expansion of BC nanocomposites with various fiber contents.

inforcement effect if compared to polyimide ($59 \times 10^{-6} \text{ K}^{-1}$)/silica nanohybrids, which resulted in just 20% reduction of CTE at a filler content of 5 wt %, accompanied by 30% degradation in transparency.^{12,13} Even when micro-sized silica particles with extremely low CTE of $0.5 \times 10^{-6} \text{ K}^{-1}$ were mixed with cyanate ester resin ($68 \times 10^{-6} \text{ K}^{-1}$) up to 70 wt %, the reduction of CTE against filler content was linear and resulted in 34% of the CTE of the matrix.¹⁴ On the other hand, BC nanocomposites' CTEs drastically decreased to $15 \times 10^{-6} \text{ K}^{-1}$ up at around 30 wt % fiber content and then gradually declined to $10 \times 10^{-6} \text{ K}^{-1}$ above 50 wt % fiber content, which is only 12% of the original acrylic resin (Fig. 3). It should be pointed out that the nanofiber network of BC might play an important role in the drastic reduction of CTE.

In conclusion, we produced bacterial cellulose nanocomposites with a wide range of fiber contents, from 7.4 to 66.1 wt %, by the combination of heat drying and or-

ganic solvent exchange methods. The addition of bacterial cellulose nanofibers linearly decreased the regular transmittance of the nanocomposites; however, the deterioration of light transmittance was limited to just 13.7% at a fiber content of 66.1 wt %. The coefficient of thermal expansion was drastically suppressed by the addition of the nanofibers. The addition of only 7.4 wt % of BC nanofibers, which deteriorated light transmittance by only 2.4%, could reduce the CTE of acrylic resin from 86×10^{-6} to $38 \times 10^{-6} \text{ K}^{-1}$, and a coefficient of thermal expansion of $15 \times 10^{-6} \text{ K}^{-1}$ was attained at 30.8 wt % fiber content.

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